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(54) Battery separators

(57) A battery separator material particularly adaptable for use in maintenance free batteries. The battery separator material includes diatomaceous earth filler, acrylate

copolymer binder and a combination of fibres comprising polyolefin, polyester and glass fibres, and has a total pore volume greater than 65%, an average pore size of 14 microns or less and an ohmic resistance of 0.015 ohms per in<sup>2</sup> or less.

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# SPECIFICATION Battery separators

This invention relates to battery separator materials, and especially to relatively inexpensive, non-cellulosic, low ohmic resistance, maintenance free battery separators.

5 Compact portable electrolytic cells or batteries including spaced apart metal plates connected in series for storage of electrical energy are well known to the art. An important factor involved in the development of such batteries is the use of thin, porous separators placed between alternating positive and negative plates. The primary function assigned the separator is to effectively prevent metallic conduction between the plates to avoid short circuiting. At the same time, the separator must permit 10 free passage of electrolyte solution for effective ion exchange between the plates.

Commercial separators have been manufactured from wood, microporous rubber, fibrous glass mats, microporous plastics, cellulosic and fibrous materials impregnated with acid insoluble resins and synthetic and glass woven fibrous and porous vitreous materials. Additional details relating to battery separators can be found in U.S. Patent Nos. 2793398; 3890184; 4024323; 4055711; 4113927; 15 3753784; 3694265; 3773590; 3351495; 3340100; 3055966; 3205098 and 2978529.

The growing evolution of the so-called "maintenance free" battery has presented special considerations and problems in the development of battery separators. The maintenance free battery is a sealed unit which does not require addition of water during the life of the battery. For many years, the separator industry has preferentially produced cellulosic separators impregnated or treated with phenol 20 aldehydes. Phenol aldehyde impregnated cellulosic separators are described in detail in U.S. Patents 3272657 and 3247025. These cellulosic separators presented an especially desirable combination of commercially attractive features including excellent electrical performance characteristics, low cost and good physical manufacturing properties. However, the outgassing properties of the cellulosic/phenolic type separator present problems in the maintenance free battery and this property 25 has effectively disqualified phenol aldehyde impregnated cellulosic separators for use in permanently sealed units. Additionally, there has been a recent increase in environmental concern in the industry with the use of phenolic aldehydes.

Alternative separators have been developed by the industry for the maintenance free battery. However, these alternative separators have not presented the attractive combination of commercial 30 features which led to the wide-spread acceptance and use of the earlier phenol aldehyde impregnated cellulosic separators. Instead, the alternative separators are generally associated with one or more commercially unattractive features such as high cost, and/or inferior electrical characteristics and/or poor physical properties and/or the use of materials of fabrication which are leachable or oxidisable thereby providing high chemical oxidation demand (C.O.D.).

35 In the development of alternative separators, particular emphasis has been placed on non-cellulosic separators providing good oxidation resistance and low ohmic resistance. The resistance to the passage of the electric current through the separator is an important factor, and is generally associated with the total porosity of the separator. As an approximation, the porosity may be assumed to be inversely proportional to the ohmic resistance. However, the manner in which porosity is achieved is 40 also of special importance. The smaller the pore size, the more the tortuosity of the path of the electrolyte through the separator, thereby reducing the opportunity for formation of metallic deposits through the thickness of the separator which can cause a direct short. Porosity is achieved in most rubber and plastic type separators—whether formed by coagulation or extrusion techniques—by including small particles in the matrix which can be leached out by appropriate solutes after formation 45 of the separator. This process provides a suitable degree of porosity but is intrinsically both costly and time consuming. In fibrous sheet separators, porosity is usually controlled by the selection of a variety of fibre diameters to regulate the size of the pores created at the interstices of the fibre crossover points and also by including relatively small amounts of siliceous type fillers. Separators providing high pore volumes can be achieved by this technique. However, the pore size and average pore sizes is 50 somewhat larger than desired.

One of the objects of the present invention is to provide a low cost, high performance, non-cellulosic separator, especially suitable for maintenance free batteries.

The invention provides a battery separator which is acid wettable but not water wettable and which comprises a substantially uniform mixture of from 10 to 20 percent by weight of the separator of 55 polyolefin fibre, from 2 to 8 per cent by weight of polyester fibre, from 0 to 15 percent by weight of glass fibre, from 50 to 75 percent by weight of diatomaceous earth and from 7 to 15 percent by weight of an acrylate copolymer binder, the separator having a total pore volume greater than 65 percent with an average pore size of 14 microns or less and an ohmic resistance of 0.015 ohms per in<sup>2</sup> or less.

The invention also provides a method for forming a battery separator material which comprises 60 the steps of:

a. Forming an aqueous dispersion which comprises polyolefin fibre in an amount sufficient to provide between 10 and 20 percent by weight of polyolefin fibre in the final separator material, polyester fibre in an amount sufficient to provide between 2 and 8 percent by weight of polyester fibre in the final separator material, glass fibre in an amount sufficient to provide between 0 and 15 percent

plastic

microporous  
adhesive

filler

by weight of glass fibre in the final separator material, diatomaceous earth in an amount sufficient to provide between 50 and 75 percent by weight of diatomaceous earth in the final separator material and an acrylate copolymer binder in an amount sufficient to provide between 7 and 15 percent by weight of binder in the final separator sheet material,

- 5 b. stabilising said aqueous dispersion in the presence of an anionic dispersing agent to form an aqueous dispersion of substantially non-flocculated agglomerates comprising said polyolefin fibre, polyester fibre, glass fibre, diatomaceous earth and binder, 5
- c. conveying the dispersion of step b. to a porous support for receiving the dispersion,
- 10 d. adding a cationic flocculating agent to said conveyed dispersion before delivering said dispersion to said porous support, 10
- e. distributing and draining the dispersion provided by step d. on said porous support, to form a wet web and
- f. drying the web.

- 15 In accordance with the practice of the invention, a preferred combination of selected materials provides a low cost, non-cellulosic battery separator having an acid wettability of under five seconds exposure time, a total pore volume exceeding 65%, conveniently about 70%, and providing an average pore size below about 14 microns preferably from about 8 to about 14 microns, a low chemical oxygen demand and an ohmic resistance below about 0.015 ohms per in<sup>2</sup>. The battery separator materials of this invention are especially adaptable for use as separators in maintenance free batteries. 15

- 20 The battery separators of this invention comprise a selected combination of fibrous materials, filler material and binder material(s). The fibrous materials include a combination of polyolefin fibres, polyester fibres and glass fibres and the composition of the separator material is presented in more detail below: 20

	Percent by weight in separator		
	Range	Preferred range	
25 Polyolefin fibre	10—20	12—16	25
Polyester fibre	2—8	4—7	
Glass fibre	0—15	12—14	
30 Filler	50—75	50—60	30
Binder	7—15	8.5—14	

- 35 Polyolefin fibres comprise a portion of the fibrous materials of battery separators of the invention. The preferred polyolefin fibres are polyolefin pulp fibres synthesized from the polymerisation of ethylene and/or propylene or mixtures thereof to provide polyethylene, polypropylene or copolymers of ethylene and propylene. Preferably, the polyolefin pulp fibres have fibre diameters from about 0.01 to about 20 microns, a softening point below about 340°F (about 171°C) and are up to about 0.5" (about 12.7 mm) in length. 35

- The polyolefin fibres most suitable in the practice of the invention are those which are characterised as synthetic wood fibres and have a surface treatment which provides improved wettability and dispersability in water. Additional properties of the preferred polyolefin fibres are (1) a surface tension of about 70 mN/m; (2) a specific gravity of less than one and preferably between about 0.900 to about 0.965 kg/dm<sup>3</sup>; (3) a melting point from about 250 to about 340°F (about 121 to about 171°C); (4) a yield stress greater than 300 daN/cm<sup>2</sup>, (5) a tensile strength at break of greater than 200 daN/cm<sup>2</sup>; (6) a modulus of elasticity in tension of from about 7000 to about 20,000 daN/cm<sup>2</sup> and (7) a dielectric constant of about 2 to about 4, a dielectric strength of about 2 to about 5 × 10<sup>2</sup> kv/cm, and a transverse resistivity of about 10<sup>15</sup> to about 10<sup>18</sup> Ωcm. The polyolefin fibres are used in amounts to provide from 10 to 20 percent by weight of the total weight of the finished separator and preferably in amounts to provide from about 12 to about 16 percent by weight. 45

- Polyester fibres are included in the battery separator materials of the invention. The polyester fibres are acid resistant and improve the overall strength of the separator particularly the puncture resistance and tear strength of the separator materials. The most preferred fibres are polyethylene terephthalate fibres having a denier from about 0.5 to about 2.2 and a length of at least about 1/4 inches (about 6.2 mm) and preferably from about 1/4 inches (about 6.2 mm) to about 3/4 inches (about 19.1 mm). The polyester fibres are used in amounts to provide from 2 to 8 and preferably from 4 to about 7 percent by weight of the total weight of the separator. A surfactant may be carried out otherwise associated with the surface of the polyester fibre to improve the dispersability of the fibre in water. 50

- 55 Acid resistant glass fibres (so-called "Chemical Grade") are preferably included in the separators of this invention to improve the wettability and wicking action of the separator and to provide improved stiffness. Suitable glass fibres have diameters ranging from about 2 microns to about 15 microns and preferably from about 8 microns to about 15 microns. The length of the glass fibres may range from about 1/8 inches (about 3.1 mm) to about 3/4 inches (about 19.1 mm) and preferably from about 1/8 inches (about 3.1 mm) to about 5/8 inches (about 15.8 mm). Combinations of glass fibres having 60

different lengths and/or diameters have been suitably employed in the practice of the invention. The glass fibres are used in amounts to provide from 0 to 15 and preferably from about 12 to about 14 percent by weight of the total weight of the separator. Glass fibres which have been treated with a water dispersible finish to provide improved dispersability in water are preferred in the practice of the invention.

The filler used in battery separators of this invention is diatomaceous earth which is also known as diatomite, infusorial earth and kieselguhr. Essentially diatomaceous earth is an amorphous silica formed from the fossilized remains of single celled aquatic plants called diatoms. Diatomaceous earth is characterised by its unique microscopic structure, chemical inertness, high absorptive capacity, internal porosity and great bulk per unit weight. The diatomaceous earths are commercially available in both natural or flux calcined grades. Natural grade diatomaceous earth is somewhat softer than the flux calcined grade and the flux calcined grade is definitely preferred in the practice of this invention. Typical properties of flux calcined grade diatomaceous earths are listed below.

15	Colour (dry)	white	
	TAPPI brightness %	89—92	15
	Scum (maximum retained on 325 mesh) %	trace, 3%	
	Absorption <sup>1</sup> (water-average), lbs/100	lb 160	
	Moisture content (maximum)	1.0	
	pH	7.0	
20	Specific gravity	2.30	20
	<sup>1</sup> Gardner-Coleman method		

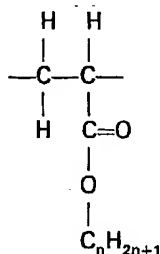
The skeletal or cellular structure of the diatomaceous earth filler provides the porosity for the separators of the invention and the cost of this porosity generating filler is relatively low. The amount of filler used is important in generating the desired degree of porosity and is sufficient to provide from 50 to 75 and preferably from about 50 to about 60 percent by weight of the total weight of the separator. The preferred amounts provide a highly filled separator having a total pore volume greater than 65%, conveniently about 70% with an average pore size less than 14 microns and where the percent of pores having a pore size greater than 20 microns is less than about 10 percent; preferably the total pore volume is between 70 and 90%. The ohmic resistance of separators of this invention—which as mentioned, is related to pore volume and pore size—is less than about 0.013 ohms in<sup>2</sup>. The above mentioned porosity is calculated by the following equation:

$$\%E = \left(1 - \frac{Pa}{Pf}\right) 100$$

where:

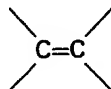
E is porosity, Pa is apparent density of the battery separator and, Pf is the columbic density of the material.

The binders included in separators of this invention are suitably self-crosslinking, non-coalescing (at room temperature) acrylate copolymers in which an acrylate moiety of the following formula represents about 80 percent or less preferably between about 80 to about 30 percent of the back-bone moieties:



where n is the integer 1—8 or somewhat higher but preferably 1—4.

Particularly suitable polymeric binders are copolymers including methyl or ethyl or butyl acrylate moieties with moieties of monomers having a



group and which provide acrylate copolymers having glass transition temperatures between about +30°C to about +60°C. The glass transition temperature (T<sub>g</sub>) are measured by Differential Thermal Analysis on a Differential Scanning Colorimeter (E. I. DuPont De Nemours Model 910) at a heating rate

of 10°C/min. Especially suitable comonomers for binders of this invention are the so-called "hard" monomers such as methyl or ethyl methacrylate and styrene or derivatives of styrene such as alpha methyl styrene. Particularly preferred binders are methyl methacrylate/acrylate copolymers.

The preferred polymeric binders are further characterised as acrylate copolymers having a surfactant(s) attached to the co-polymer molecule so as to be substantially non-leachable under the conditions of separator preparation and operation. Preferably the attached surfactant is an anionic surfactant such as a sulfo-succinate ester present in an amount from about 0.25 to about 2.5 percent by weight of the copolymer. Preferred polymeric binders of this invention are further characterised as having intrinsic viscosities from 0.8 to about 2.0 at 30°C. Intrinsic viscosities are measured on a freshly prepared copolymer latex (to minimise crosslinking effect) using an amount of the latex sufficient to provide about 0.3 to about 0.4 grams copolymer solid. The amount is placed in 100 mls dimethyl formamide, allowed to dissolve and flow rates of solution and solvent alone are measured at 30°C. in an Ostwald type viscometer.

The especially preferred acrylate copolymers are those which have a silane coupling agent attached to or included in the polymer backbone. These especially preferred acrylate copolymers are commercially available and can be prepared by copolymerising the acrylate copolymer monomers with a silane coupling agent having ethylenic unsaturation which can undergo free radical polymerisation. The amount of silane coupling agent in the acrylate copolymer can represent from about 0.2 to about 2.0 percent by weight. Especially preferred silane coupling agent containing acrylate copolymers include methyl methacrylate/acrylate copolymers and styrene/acrylate copolymers. The silane coupling agent containing acrylate copolymers provide improved internal bonding between the silaceous components (glass fibres and diatomaceous earth) of the separator. Battery separators including the preferred silane coupling agent containing acrylate copolymers exhibit especially superior resistance to corrosive acids.

Separators according to the invention comprising fibre, filler materials, and acrylate copolymer binders are acid wettable but not water wettable. By "acid wettable" is meant that a drop of sulphuric acid solution (1.2 specific gravity) placed on the surface of a separator of this invention will be substantially completely absorbed or otherwise not discernable as a drop within about five seconds or less. By "not water wettable", is meant that a drop of water placed on the surface of the separator will not be completely absorbed but will be discernable as a drop for about 30 minutes and preferably for about 60 or longer. The binder is used in amounts to provide between 7 to 15 and most preferably between about 8.5 to about 14 percent by weight of the finished separator.

The polymeric binders are used as latex dispersions which have an acid pH. In carrying out a method for forming batter separator material, according to the invention. Typical properties of separators formed with the latex dispersions include a tensile of about 8 lbs. (about 3.63 kg.) and a puncture of more than about 400 grams.

Conveniently in carrying out a method according to the invention separator material is produced by forming an aqueous dispersion of the above described fibre materials, filler material and binder material, sequentially adding dispersing and flocculating agents to the dispersion, applying the flocculated agglomerates to the wire of a web forming apparatus to provide a web product having a thickness less than about 30 mils and dewatering the product.

The preferred preparation of separator material by a method according to the invention, particularly at a pilot plant or full production scale, involves a retention aid or system which utilises a charge-reverse-charge mechanism. The procedure can be performed on standard papermaking apparatus such as fourdrinier, an inclined fourdrinier, a cylinder machine, a rotoformer or the like. According to this procedure, the pulper is first charged with water, the polyolefin fibres, the diatomaceous earth and the polyester and glass fibres. A dispersion of a heavily anionic material is then charged to the pulper. The preferred anionic material is a carboxylated acrylamide and the amount used is preferably about 0.2% by weight of the total furnish. The anionic material functions as a dispersing agent and imposes a heavy anionic charge on the fibre and filler materials. The latex binder which is also anionic in character is then added as the last ingredient. Accordingly, unlike usual beater addition procedures, no flocculation occurs in the pulper. It has been found that if flocculation of the ingredients occurs in the pulper, shear forces generated by agitation and pumping can cause the latex particles to be dislodged from their bonding sites on the fibre.

The unflocculated furnish is then charged to the machine chest of a paper making machine by way of a pump—such as a fan pump. The furnish is preferably flocculated at the fan pump by mixing a cationic flocculating agent—preferably a polyethyleneimine—with the furnish. The amount of cationic flocculating agent added to the dispersion at this point can be regulated to control the size of the flocculated agglomerates deposited on the wire which permits adjustment and/or control of drainage time and retention rate for optimum results. According to this procedure, retention rates of 97—98 percent can be achieved.

The flocculated agglomerates charged to the machine chest are transferred to the moving wire of the papermaking machine as a web for drainage of water. After draining the water by gravity, suction may be applied to remove further water from the web. The web may then be pressed between felt rolls

and dried on drying cans. Suitable drying temperatures are from about 230 to about 260°F (about 110 to about 127°C) and during drying at least some crosslinking of the binder material occurs.

Another procedure for avoiding the effect of shear forces on the materials dispersed in the pulper involves a variation of the above-described preferred preparation. According to this alternative procedure, a cationic flocculating agent is first added to the material dispersed in the pulper to obtain retention of the binder and filler. Reduction in particle size of the flocculated material by the shear forces is controlled by adding a highly anionic colloid such as deacetylated Karaya Gum after addition of the cationic flocculating agent. The anionic colloid provides a negative charge on the flocculated agglomerates which disperses the agglomerates into smaller particles which are resistant to further reduction in size in response to the encountered shearing forces. The cationic flocculating agent is reintroduced to the dispersion preferably at the fan pump and the flocculated material is charged to the machine chest, transferred to the moving cure and dried as described before. This alternative procedure is more analogous to typical beater addition procedures known to the art.

There now follows a detailed description, hereinafter set out as Examples I to IV, of battery separators and methods of making them, embodying the invention. It will be realised that these separators and methods have been selected for description to illustrate the invention by way of example.

#### Example I

The following materials were added in the sequence listed to a Williams 10" x 12" (about 254 mm x 305 mm) hand sheet mould:

	Polyolefin fibre <sup>1</sup> .	6.96 grams (42% solids)	
	Filler <sup>2</sup> .	14.4 grams (diluted to 3% consistency in water and defibred in a Waring Blender for 2 minutes)	
	Glass fibre	0.81 grams (1/4" (about 6.2 mm) x 5.6 microns)	
25	Polyester fibre <sup>3</sup> .	0.81 grams (1/8" (about 3.1 mm) x 5.6 microns)	25
		0.81 grams (defibred in Waring Blender for 20 seconds)	
	Anionic colloid <sup>4</sup> .	60 grams (at 0.1% solids)	
	Polymeric binder <sup>5</sup> .	4.05 mls (1.971 gms solid)	
30	Cationic flocculating agent <sup>6</sup> .	0.3 mls	30

<sup>1</sup>The polyolefin fibres in this and all other Examples are synthetic wood pulp fibres having an average fibre diameter of 4.9 microns and are supplied by Hercules Powder Company under the Trade Mark Pulpex EA.

<sup>2</sup>The filler used in this and all other Examples is a diatomaceous earth having a median particle size of 16 microns. The filler is supplied by Johns Mansville under the trade name Celite 110.

<sup>3</sup>The polyester fibre in this and all other Examples is a 1/4" (about 6.2 mm), 15 denier polyethylene terephthalate fibre supplied by E. I. DuPont De Nemours under the Trade Name Dacron.

<sup>4</sup>The anionic colloid used in this Example was prepared by mixing together 1.16 lbs (about 0.53 kg) of a carboxylated acrylamide sold under the Trade Name Betz DP-791 by Betz Paper Chemical Incorporated with 44.5 gallons (about 168 litres) of water. The carboxylated acrylamide anionic colloid was added by addition method and the dispersion was mixed with slow agitation until the colloid was dissolved.

<sup>5</sup>The polymeric binder used in this Example was a styrene/butyl acrylate copolymer having a silane coupling agent attached to the polymeric backbone and was supplied by National Starch and Chemical Corporation under the designation 78-6170. The binder is supplied and used as a latex dispersion and has a pH from 4.0 to 5.0, a wet weight of 8.64 lbs per gallon (about 1.027 kg/litre), a dry weight of 4.181 lbs per gallon (about 0.497 kg/litre), a percent solids of 48.0, a specific gravity of 1.036 and a Brookfield viscosity of 310 cps.

<sup>6</sup>The cationic flocculating agent used in this Example is a polyethyleneimine which is supplied by Basf Wyandotte under the Trade Name Polymine P. The flocculent was prepared by diluting 5 gallons (about 18.9 litres) of Polymine P in 45 gallons (about 170 litres) of water.

The above materials were diluted to a 1.5% consistency and drained through a 72x76 plastic wire screen. Drainage time was three (3) seconds. The sheet was wet pressed and dried.

The dried separator sheet material had the following composition:

		<i>Percent by weight of separator material</i>	
5	Polyolefin fibre	13.4	
	Polyester fibre	3.7	
	Glass fibre	7.5	5
	Diatomaceous earth	66.3	
	Binder	9.1	
10	The ohmic resistance of separators of the above composition having a sheet gauge of 0.0285" (about 0.72 mm) was measured and the following results were obtained:		
	20 minute ohmic resistance—0.0120 ohms		10
	24 hours ohmic resistance—0.0105 ohms		
	Porosity characteristics of the sheet material were determined and the following results were obtained:		
15	Total porosity	68.8466%	15
	Maximum porosity	69.0021%	
	Porosity due to pores less than 0.06223 micron diameter	0%	
	Average pore size	7.767 microns	
20	% of pores greater than 20 microns	7.5916%	20
	Acid Wet Out for the sheet material was instantaneous and the sheet material was not Water Wettable.		
	Battery cell tests with cells made with the separator material show excellent charge acceptance, cold crank performance and no degradation under an overcharge paste test.		
25	The separator material was subject to refluxing sulphuric acid dichromate solution for three hours and showed an average weight loss of from 1% to 2% maximum with no blistering or delamination occurring.		25
	<b>Example II</b>		
30	A furnish was prepared by adding the following materials to a pulper in the order listed. (The materials are the same as used in Example I):		30
	Water	2500 gallons (about 9463 litres)	
	Polyolefin fibre	260 lbs (dry) (about 118 kg)	
	Diatomaceous earth	1100 lbs (about 499 kg)	
35	Glass fibre (1/4" (about 6.2 mm)x 13.0 microns)	280 lbs (about 127 kg)	35
	Polyester fibre	100 lbs (about 45.3 kg)	
	Anionic colloid	172 gals (about 651 litres) @ 3% solids	
	Binder	62 gallons (about 235 litres)	
40	The fibre and filler materials were dispersed in the sequence noted above to provide a uniform dispersion. The fibre and filler materials were negatively charged by the addition of the anionic colloid dispersing agent. Addition of the anionically charged binder completed the pulper cycle and the dispersion was then pumped to the machine chest of a fourdrinier papermaking machine. The pump used to charge the machine chest was a fan pump and at the fan pump, the cationic flocculating agent was added to and mixed with the dispersion at a rate of about 48 gallons (about 182 litres) per hour.		40
45	Water was added to maintain the dispersion in the machine chest at a consistency of about 1.2%. The dispersion was fed onto the moving screen of the fourdrinier to provide a web, water was allowed to drain by gravity and then suction was applied to the web. The wet web was then passed between a roll over felt press and then dried by passing it over heated rolls to heat the web to about 255°F (about 124°C).		45
50	The dried separator sheet material had the following composition:		50
		<i>Percent by weight of separator material</i>	
55	Polyolefin fibre	12.87	
	Polyester fibre	6.93	
	Glass fibre	13.86	55
	Diatomaceous earth	54.45	
	Binder	12.7	

A battery separator prepared as described had the following properties:

	Property	Value	
	Backweb $t_b$ ins	0.027 (about 0.69 mm)	
	Overall $t_b$ ins	0.045 (about 1.14 mm)	
5	Weight/area $g/m^2$	238	5
	Ohmic resistance		
	20 mins $in^2$	0.016	
	Ohmic resistance		
	24 hours $in^2$	0.014	
10	48 hours $in^2$	0.013	10
	Apparent density <sup>1</sup>	0.3952	
	% porosity	74	
	Pore diameter avg in microns	14	
	% volume greater than 20 microns	20	
15	Gradient columnar density %	1.74	15
	Tensile strength lbs	16.2 (about 7.35 kg)	
	% elongation	1.0	
	Acid wettability	Instantaneous	
	Water wettability	60+ minutes	
20	COD	1400 ppm	20
	Puncture resistance	Greater than 600 grams	

<sup>1</sup>Measured on an Aminco Mercury Porosimeter under liquid mercury pressure.

The battery separator was used in a lead-acid storage battery and tested for performance according to the Battery Counsel Industry (BCI) recommended specifications for vehicular, ignition lighting and starting types. The results are as follows:

Discharge performance characteristics			
	Reserve capacity 25 amps at 80°F (about 26.7°C)		
	minutes to 10.5 volts	64.6 minutes	
	Cold crank 450 amps at 0°F (about -17.8°C)		
30	voltage at 30 sec	8.16 volts	30

The battery separators of Examples I and II include the especially preferred acrylate copolymer having a silane coupling agent attached to or included in the polymer backbone. Separators containing the especially preferred acrylate copolymers exhibit superior resistance to corrosive acids and this is an important performance characteristic for maintenance free battery separators. As those in the art know, a battery undergoes plate formation via an electrical charge during construction. Frequently during such plate formation, charging conditions may be inadvertently exceeded leading to higher than desired temperatures in the battery. Currently available maintenance free battery separators tend to blister or delaminate under these temperature conditions, resulting in short circuiting of the plates. A test to determine the propensity of a separator to delaminate or blister under the above described conditions involves refluxing a sample of the separator in a sulphuric acid dichromate solution for three hours. After refluxing, the sample is examined to determine if blistering or delamination has occurred and the degree of blistering or delamination which has occurred. Separators of Examples I and II show no blistering or delamination under these test conditions.

#### Example III

The following materials were added in the sequence listed to a Williams 10"×12" (about 254 mm×305 mm) hand sheet mould:



	Polyolefin fibre	6.96 grams (42% solids)	
	Filler	14.4 grams (diluted to 3% consistency in water and defibred in a Waring Blender for 2 minutes)	
5	Glass fibre	0.81 grams (1/4" (about 6.4 mm) x 5.6 microns)	
	Polyester fibre	0.81 grams (1/8" (about 3.2 mm) x 5.6 microns)	5
		0.81 grams (defibred in Waring Blender for 20 seconds)	
	Cationic flocculating agent <sup>7</sup>	0.3 ml	
10	Polymeric binder <sup>8</sup>	4.05 mls (1.971 gms solid)	
	Anionic colloid <sup>9</sup>	10 grams (0.1 gms solid)	10

<sup>7</sup>The cationic flocculent used in this Example is a polyamine which is supplied by Betz Corporation under the trade name Betz 1285. The flocculent was prepared by diluting a gallon (about 3.79 litres) of Betz 1285 in 50 gallons (about 189 litres) of water.

<sup>8</sup>The polymeric binder used in this Example was a styrene/butyl acrylate copolymer supplied by National Starch and Chemical Corporation under the designation 78-6132. The binder is supplied and used as a latex dispersion and has a pH of 4.9, a wet weight of 8.64 lbs per gallon (about 1.027 kg/litres), a dry weight of 4.181 lbs per gallon (about 0.497 kg/litres), a percent solids of 48.4, a specific gravity of 1.036 and a Brookfield viscosity of 310 cps.

<sup>9</sup>The anionic colloid used in this Example was prepared by mixing together the following materials:

20	Water 60°C	33 1/3 gallons (about 126 litres)	
	Tiethanolamine	17.5 cc	20
	Ammonia	300 cc	
	Karaya Gum Powder	4.5 lbs (about 2.04 kg)	

25 Cold water was then added to increase the volume to 50 gallons (about 189 litres). The weight of Karaya Gum Powder in the dispersion was 1% by weight.

The above materials are diluted to a 1.5% consistency and drained through a 72 x 76 plastic wire screen. Drainage time was three (3) seconds. The sheet was wet pressed and dried.

The dried separator sheet material had the following composition:

30		<i>Percent by weight of separator material</i>	30
	Polyolefin fibre	13.4	
	Polyester fibre	3.7	
	Glass fibre	7.5	
35	Diatomaceous earth	66.3	35
	Binder	9.1	

The ohmic resistance of separators of the above composition having a sheet gauge of 0.0285" (about 0.72 mm) was measured and the following results were obtained:

40	20 minute ohmic resistance—0.0120 ohms		
	24 hour ohmic resistance—0.0105 ohms		
	Porosity characteristics of the sheet material were determined and the following results were obtained:		40

45	Total porosity	68.8466%	
	Maximum porosity	69.0021%	
	Porosity due to pores less than 0.06223 micron diameter	0%	45
	Average pore size	7.767 microns	
	% of pores greater than 20 microns	7.5916%	

50 Acid Wet Out for the sheet material was instantaneous and the sheet material was not Water Wettable.

Battery cell tests with cells made with the separator material show excellent charge acceptance; cold crank performance and no degradation under an overcharge paste test.

The separator material was subject to refluxing sulphuric acid dichromate solution for three hours and showed an average weight loss of from 1% to 2% maximum.

#### 55 Example IV

The same amounts of the same fibre materials, filler, cationic flocculent and anionic colloid as in Example III were used to prepare Separators A, B, C, D, E and F of this Example. However, the binder

material used in prepared the Separators of this Example was different and the amount used was sufficient to provide 9, 10, 11, 12, 13 and 14 percent by weight of binder in Separators A, B, C, D, E and F respectively. The different binder material used in this Example is a methyl methacrylate/butyl acrylate copolymer supplied by National Starch and Chemical Corporation under the designation 78-6139. The binder is supplied and used as a latex dispersion and has a pH of 4.2, a wet weight of 8.94 lbs per gallon (about 1.063 kg/litre), a dry weight of 4.326 lbs, per gallon (about 0.514 kg/litre), a percent solids of 48.4, a specific gravity of 1.070 and a Brookfield viscosity of 310 cps. The ohmic resistance of the Separators are listed in tabular form below:

Table 1

Separator	% by weight binder	20 minutes ohmic resistance	24 hour ohmic resistance
A	9	0.0100	0.0090
B	10	0.0104	0.0100
C	11	0.0104	0.0090
D	12	0.0125	0.0100
E	13	0.0114	0.0110
F	14	0.0120	0.0114

Acid Wet Out for each Separator material of Table 1 was instantaneous and each Separator was not Water Wettable.

Battery cell tests with each Separator of Table 1 show excellent charge acceptance, cold crank performance and no degradation under an overcharge plate test.

Average weight losses for each Separator of Table 1 after three hours if immersion in refluxing sulphuric acid dichromate solution were 1% to 2% maximum.

From the above description, it will be apparent that this invention presents to the art novel, improved, acid wettable, non-cellulosic battery separators particularly adaptable for use in maintenance free batteries. Moreover, the separators present the distinctive combination of excellent electrical performance characteristics, low material and production costs and good physical properties and manufacturing features. The separators have low ohmic resistance, low chemical oxygen demand and excellent porosity characteristics in terms of pore volume and low average pore size generated by using a large amount of a relatively inexpensive filler. Accordingly, the novel separators of this invention provide unexpected advantages in terms of overall performance characteristics, cost and manufacture as compared to those known to the art at the time the invention was made.

#### Claims

1. A battery separator which is acid wettable but not water wettable and which comprises a substantially uniform mixture of from 10 to 20 percent by weight of the separator of polyolefin fibre, from 2 to 8 percent by weight of polyester fibre, from 0 to 15 percent by weight of glass fibre, from 50 to 75 percent by weight of diatomaceous earth and from 7 to 15 percent by weight of an acrylate copolymer binder, the separator having a total pore volume greater than 65 percent with an average pore size of 14 microns or less and an ohmic resistance of 0.015 ohms per in<sup>2</sup> or less.

2. A battery separator according to claim 1 where the total pore volume is about 70 percent.

3. A battery separator according to claim 1 where the total pore volume is between 70 and 90 percent.

4. A battery separator according to any one of the preceding claims which comprises from 12 to 16 percent by weight of polyolefin fibre, from 3 to 8 percent by weight of polyester fibre, from 5 to 15 percent by weight of glass fibre, from 50 to 70 percent by weight of diatomaceous earth and from 8.5 to 14 percent by weight of binder.

5. A battery separator according to any one of the preceding claims where the binder is a copolymer of methyl acrylate or ethyl acrylate or propyl acrylate or butyl acrylate or mixtures of these.

6. A battery separator according to any one of claims 1 to 4 wherein the binder is a copolymer of methyl methacrylate and ethyl acrylate, methyl methacrylate and butyl acrylate, styrene and ethyl acrylate, styrene and butyl acrylate, or mixtures of these.

7. A battery separator according to any one of the preceding claims where the copolymer binder includes a silane coupling agent attached to the polymeric backbone.

8. A battery separator according to any one of the preceding claims where the diatomaceous earth is a flux calcined grade diatomaceous earth.

9. A method for forming a battery separator material which comprises the steps of:

a. forming an aqueous dispersion which comprises polyolefin fibre in an amount sufficient to provide between 10 and 20 percent by weight of polyolefin fibre in the final separator material, polyester fibre in an amount sufficient to provide between 2 and 8 percent by weight of polyester fibre in the final separator material, glass fibre in an amount sufficient to provide between 0 and 15 percent

- by weight of glass fibre in the final separator material, diatomaceous earth in an amount sufficient to provide between 50 and 75 percent by weight of diatomaceous earth in the final separator material and an acrylate copolymer binder in an amount sufficient to provide between 7 and 15 percent by weight of binder in the final separator sheet material,
- 5 b. stabilising said aqueous dispersion in the presence of an anionic dispersing agent to form an aqueous dispersion of substantially non-flocculated agglomerates comprising said polyolefin fibre, polyester fibre, glass fibre, diatomaceous earth and binder, 5
- c. conveying the dispersion of step b. to a porous support for receiving the dispersion,
- d. adding a cationic flocculating agent to said conveyed dispersion before delivering said
- 10 dispersion to said porous support, 10
- e. distributing and draining the dispersion provided by step d. on said porous support, to form a wet web and
- f. drying the web.
10. A method according to claim 9 where the amount of polyolefin fibre is sufficient to provide
- 15 from 12 to 16 percent by weight of polyolefin fibre in the final separator materials, the amount of polyester fibre is sufficient to provide from 5 to 8 percent by weight of polyester fibre in the final separator material, the amount of glass fibre is sufficient to provide from 10 to 15 percent by weight of glass fibre in the final separator material, the amount of diatomaceous material is sufficient to provide
- 20 from 50 to 60 percent by weight of diatomaceous earth in the final separator material and the amount of acrylate copolymer binder is sufficient to provide from 8.5 to 14 percent by weight of binder in the final separator material. 20
11. A method according to either one of claims 9 and 10 where the copolymer binder is a copolymer of methyl acrylate or ethyl acrylate or propyl acrylate or butyl acrylate or mixtures of these.
12. A method according to either one of claims 9 and 10 where the copolymer binder is a
- 25 copolymer of methyl methacrylate and ethyl acrylate, methyl methacrylate and butyl acrylate, styrene and ethyl acrylate, styrene and butyl acrylate or mixtures of these. 25
13. A method according to any one of claims 9 to 12 where the copolymer binder includes a silane coupling agent attached to the polymeric backbone.
14. A method according to any one of claims 9 to 13 where the diatomaceous earth is a flux
- 30 calcined grade diatomaceous earth. 30
15. A method according to any one of claims 9 to 14 where the anionic dispersing agent is a carboxylated acrylamide.
16. A method according to any one of claims 9 to 15 where the cationic flocculating agent is a polyethyleneimine.
17. A method according to anyone of claims 9 to 16 where a cationic flocculating agent is added
- 35 to the dispersion of step a. prior to stabilising said dispersion according to step b. 35
18. A battery separator constructed arranged and adapted to operate substantially as hereinbefore described with reference to any one of Examples I to IV.
19. A method for forming a battery separator material substantially as hereinbefore described
- 40 with reference to any one of Examples I to IV. 40
20. In a battery with an electrolyte and a positive plate and a negative plate separated by a battery separator, the improvement where said separator is a separator according to any one of claims 1 to 8 and 18.